



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 301 837
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 88306929.6

(51) Int. Cl. 4: C 10 L 1/14

(22) Date of filing: 27.07.88

(30) Priority: 28.07.87 JP 186651/87

(43) Data of publication of application:
01.02.89 Bulletin 89/05

(84) Designated Contracting States: DE FR GB NL

(71) Applicant: SUMITOMO CHEMICAL COMPANY, LIMITED
15 Kitahama 5-chome Higashi-ku
Osaka-shi Osaka 541 (JP)

(72) Inventor: Ohmae, Tadayuki
10-2-409 Inagehigashi 6-Chome
Chiba-shi Chiba (JP)

Hara, Sumio
9-11 Nagauraekimae 2-Chome Sodegaura-machi
Kimitsu-gun Chiba (JP)

Mashita, Kentaro
9-3 Aobadai 4-Chome
Ichihara-shi Chiba (JP)

(74) Representative: Holdcroft, James Gerald, Dr. et al
Graham Watt & Co. Riverhead
Sevenoaks Kent TN13 2BN (GB)

(54) Flow-improved fuel oil composition.

(57) A fuel oil composition is disclosed, which comprises a base fuel oil composed mainly of middle and/or heavy distillates of crude oil and containing n-paraffin having at least 25 carbon atoms in an amount of not smaller than 0.1 wt.% and smaller than 0.6 wt.% and wax which separates out at a temperature by 10°C lower than the cloud point in an amount of smaller than 4 wt.%, and a cold flow improver composed of a copolymer of ethylene and a vinyl ester of an unsaturated carboxylic acid, the copolymer having an ethylene content of 60 to 80 wt.% and a number average molecular weight of 1,000 to 5,000, in an amount of 30 to 1,500 ppm.

Presence of the specific ethylene-vinyl acetate copolymer based cold flowability improver and limited content of specific n-paraffin improves cold flowability of fuel oils.

EP 0 301 837 A1

Description

FLOW-IMPROVED FUEL OIL COMPOSITION

5

BACKGROUND OF THE INVENTION

a) Field of the Invention

10 This invention relates to a fuel oil composition having a low flowability at low temperatures prepared from a heavy distillate fuel of petroleum and a low temperature flow improver.

b) Prior Art

15 As is well known, among fractions obtained by distilling crude oil, those called as middle and heavy fractions and having boiling points from about 150 °C to 450 °C respectively, are used extensively as various fuel sources such as kerosene, gas oil, and heavy oil A.

20 Particularly, kerosene and heavy oil A suffer remarkable decrease in flowability at low temperatures (or cold flowability) in winter season and the like due to separation of wax component contained in the oil, which tends to cause severe problems.

25 For example, under cold conditions of winter season, the wax component contained in kerosene separates out and causes clogging or plugging of minute screen which is incorporated in a filter for preventing impurities provided in midway in a pipeline from a kerosene tank to an engine in a diesel automobile, so that supply of kerosene becomes impossible and as the result the engine stops. Under much lower temperature conditions, kerosene as a whole gels to lose flowability.

30 Separation of wax component occurs also in heavy oil A, which is used widely for driving engines in fishing boats, for warming greenhouses used in order to accelerate cultivation as well as for heating buildings, resulting in incomplete combustion which gives a serious influence to humans and plants.

35 Various measures have heretofore been taken in order to maintain sufficient flowability of fuel oil at low temperatures.

40 For example, a method is known in which fuel oil is heated with warm water or with an electric heater in order to prevent decrease in the temperature of the fuel oil due to decrease in the ambient temperature, and to keep the temperature of the fuel oil at certain temperature range. However, this method is practically disadvantageous because it requires amelioration or reconstruction of installations and incur additional cost for energy.

45 Also, it is known to dilute fuel oils with those fractions which retain cold flowability at relatively low temperatures, e.g., kerosene fractions. This method is not suitable because relatively light fuel oils to which the kerosene fractions belong are in great demand and highly value-added.

50 Another conventional method for improving the cold flowability of fuel oils is to add a cold flow improver to the fuel oils.

The action of the cold flow improver is to give influence upon separation-out of wax from fuel oils to prevent the growth of wax into large-size crystals but retain the wax in the form of minute crystals, thus stabilizing the cold flowability.

55 Various synthetic chemicals have been proposed as a cold flow improver. However, their effect vary extremely depending on the characteristics of fuel oils to which they are added; it is very important to grasp the characteristics of fuel oils which can be subjected to quality control steadily. However, this is very difficult because there are a great variety of crude oil types very complicated operational conditions of distilling apparatus and other factors are involved.

60 In order for the cold flow improver to virtually exhibit its effect upon addition, various considerations have been taken on the characteristics of the fuel oils concerned.

For example, Published Unexamined Japanese Patent Application No. Sho-58-134188 describes improvement in the cold flowability of a middle fraction fuel oil by adding 0.2 to 1.5 parts by weight of an ethylene copolymer and n-paraffin having 26 to 27 carbon atoms to 100 parts by weight of the fuel oil.

55 This method not only requires addition of both the ethylene copolymer and n-paraffin, which causes complication of installations and operation, but also involves increase in the amount of wax separated out at low temperatures because of paraffin, which is a principal causal substance for aggravation of cold flowability due to separating-out of wax, is positively added. As the result, it is often the case that the cold flow improver does not act effectively.

60 In a typical utility where fuel oil is used as a fuel for driving a Diesel engine automobile, fuel oil is passed in a fuel supply pipeline in the midway of which is provided with a strainer which tends to cause early plugging because of separation-out of wax in great amounts, resulting in shortened wax saturation time. Therefore, this solution involving provision of strainer is undesirable.

Published Unexamined Japanese Patent Application No. Sho-61-58116 discloses a composition containing gas oil of which the content of paraffin wax that separates out at a temperature of -20°C is adjusted to a level of from 5.5 to 12 wt.% and a pour point depressant.

However, this proposal is insufficient because even with gas oil of which the content of paraffin wax separating out at -20°C is specifically adjusted to a range of from 5.5 to 12 wt.%, it sometimes happens that the addition of a pour point depressant fails to decrease CFPP (cold filter plugging point) at all, and that decrease of CFPP cannot be achieved until a specified pour point depressant is added. 5

As described above, it has conventionally been difficult to provide fuel oils of which cold flowability has been improved steadily because the prior art additives are effective only to fuel oils having specific characteristics or because a large amount of a specific substance other than the additive must be added in order to facilitate exhibition of the effect of the prior art additives. 10

SUMMARY OF THE INVENTION

Therefore, an object of this invention is to obviate the above-described defects of the prior arts and provide a fuel oil mainly composed of medium and/or heavy distillates of crude oil and having an improved cold flowability. 15

Another object of this invention is to optimize the amount of n-paraffin contained in the middle and/or heavy distillates of crude oil in order to have sufficiently exhibited the effect of a cold flow improver.

As a result of extensive research, this invention has been completed, which provides a fuel composition comprising a base fuel oil composed mainly of middle and/or heavy distillates of crude oil and containing n-paraffin having at least 25 carbon atoms in an amount of not smaller than 0.1 wt.% and smaller than 0.6 wt.% and wax which separates out at a temperature by 10°C lower than the cloud point in an amount of smaller than 4 wt.%, and a cold flow improver composed of a copolymer of ethylene and a vinyl ester of an unsaturated carboxylic acid, the copolymer having an ethylene content of 60 to 80 wt.% and a number average molecular weight of 1,000 to 5,000, in an amount of 30 to 1,500 ppm. 20 25

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a graph representing gas chromatogram of test oil No.5 obtained by the technique of gas chromatographic n-paraffin analysis according to example, with the portions calculated as n-paraffin being shadowed with oblique lines. 30

Fig. 2 is a graph showing relationship between the content of n-paraffin having at least 25 carbon atoms contained in various test oils and decrease in the cold filter plugging point (Δ CFPP) upon the addition of 500 ppm of Additive A, i.e., a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 36.5 wt.% and a number average molecular weight of 1,690. 35

Fig. 3 is a graph showing relationship between the content of n-paraffin having at least 25 carbon atoms contained in various test oils and decrease in the cold filter plugging point (Δ CFPP) upon the addition of 500 ppm of Additive B, i.e., a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 16.5 wt.% and a number average molecular weight of 2,200. 40

Fig. 4 is a graph showing relationship between the content of n-paraffin having at least 25 carbon atoms contained in various test oils and decrease in the cold filter plugging point (Δ CFPP) upon the addition of 500 ppm of Additive C, i.e., a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 44.6 wt.% and a number average molecular weight of 1,820. 45

DETAILED DESCRIPTION OF THE INVENTION

In this invention, the term "base fuel oil composed mainly of middle and/or heavy distillates of crude oil" used herein refers to distillate oils obtained by distilling crude oil which is a mixture of a great number of components composed mainly of hydrocarbons having a boiling point of from about 150°C. to about 450 °C. 50

Examples of distillate fractions obtained from general petroleum distilling installations include light gas oil, heavy gas oil, or heavy gas oil hydrogenated using a purifier such as a unifiner, or vacuum gas oil which is obtained by vacuum distilling the distillation residue from normal pressure distillator in a vacuum distillator and its hydrogenated product. They can be used as a blend depending on their application. 55

If necessary, the base fuel oil can be mixed with a small amount of middle or heavy distillate oil generated in petroleum purifiers, e.g., oils treated in catalytic cracking apparatus, hydrogenolysis apparatus, etc. or residual oils after dewaxing during manufacture of lubricants. 60

Further, it can be mixed with a small amount of normal pressure residual oil or vacuum residual oil or extracted oil generated during the step of purification of lubricants, as is generally adopted as a method for adjusting heavy oil A.

In this invention, the amount of n-paraffin having at least 25 carbon atoms contained in the middle and/or

heavy distillate oils of petroleum as base fuel oil can be analyzed in a usual manner using a programmed-temperature gas chromatography apparatus.

More particularly, a trace amount sample is analyzed using a hydrogen flame ionizing detector with a column packed with a filler composed of a partition agent having a weak polarity and a porous carrier, and the content of n-paraffin is obtained from the respective chromatograms of the separated components.

For example, a sample oil is injected into a column of a stain-less steel tube having a diameter of 3 mm and a length of 4,000 mm packed with a column filler (Silicon GE SE-30, 2%, 60/80 mesh, Uniport HP carrier) commercially available from Wako Pure Chemicals Industries, Ltd. and the temperature of the column is elevated starting from 70°C to 270 °C at a rate of 5 °C/min., and detection is performed by hydrogen flame ionizing method. The electric signals detected are processed with a recorder or data processor as output to outside. The content of n-paraffin can be obtained by calculating n-paraffin peak.

In this invention, the content of n-paraffin having at least 25 carbon atoms contained in the middle and/or heavy distillate oils of petroleum as base fuel oil is preferably not smaller than 0.1 wt.% and smaller than 0.6 wt%.

When the content of n-paraffin having at least 25 carbon atoms is smaller than 0.1 wt%, the effect of improvement in cold filter plugging point with a cold flow improver becomes poor. On the other hand, when it is larger than 0.6 wt%, although sometimes addition of a very large amount, e.g., 2,000 ppm or more, of a cold flow improver permits improvement in cold filter plugging point, total amount of wax which separates out increases, resulting in that the fuel oil obtained tends to be one which cannot be used practically.

Preferred amount of n-paraffin having at least 25 carbon atoms with which the effect of cold flow improver added can be exhibited more efficiently is not smaller than 0.2 wt.% and smaller than 0.5 wt%. In this range, addition of a relatively low amount of cold flow improver enables sufficient decrease in the cold filter plugging point.

Examples of the cold flow improver used in this invention include those described in "Shinpan Seklyu Seihin Tenkazai" ed. by Toshio Sakurai, Salwal Shobo, July 1986, pp.192-195. More particularly, ethylene copolymers disclosed in Japanese Patent Publication Nos. Sho-48-23165, Sho-55-33480, and Sho-60-17399, Published Unexamined Japanese Patent Application No. Sho-59-136391.

Examples of the ethylene copolymer include those copolymers which contain one or more vinyl esters of saturated fatty acids such as vinyl acetate, vinyl propionate, vinyl butyrate, etc. as a comonomer. They may be a low molecular weight product obtained by decomposing a high molecular weight ethylene copolymer with oxygen, peroxides, heat, etc.

Preferred ethylene copolymer includes those copolymers which have an ethylene content of 60 to 80 wt.%, and a number average molecular weight in the range of from 1,000 to 5,000 measured by vapor pressure equilibrium method.

When the ethylene content is below 60 wt.% or not lower than 80 wt.%, or the number average molecular weight is below 1,000 or not lower than 5,000, the effect of improvement in cold filter plugging point is rather poor and a large amount of the improver must be added, which is not advantageous from economical viewpoint.

The ethylene copolymer may be used singly or as a mixture of two or more of it. Although the ethylene copolymer can be mixed with and dissolved in fuel oils as it is, it is industrially preferred to dissolve it in a hydrocarbon based solvent and use it as a 10 to 90 wt.% solution.

Among the ethylene copolymers described above, ethylene-vinyl acetate copolymers are particularly preferred because they are not only readily available on industrial scale but also are excellent in the effect of improving cold flowability.

More preferred ethylene-vinyl acetate copolymer is those copolymers having an ethylene content of 60 to 75 wt.%, and a number average molecular weight of 1,000 to 4,000, with molecular weight distribution being not lower than 4.0, and containing not more than 6 methyl terminated side chains per 100 main-chain methylene groups as well as methyl groups contained in the acetyl group. The copolymers exhibit further decrease in cold filter plugging point.

The molecular weight distribution is obtained from the ratio of weight average molecular weight (M_w)/number average molecular weight (M_n) calculated as standard polystyrene according to gel permeation chromatography (GPC) (cf. "Kobunshi Sokuteihou, Kouzou to Bussei" vol. 1, ed. by Kobunshi Gakkai, Baihukan, 1973, pp.76-89).

Further, the degree of branching as used herein is expressed as the number of methyl terminated side chains per 100 main-chain methylene groups besides methyl groups in the acetoxy groups, and calculated from the results obtained by nuclear magnetic resonance ($^1\text{H NMR}$) method (cf. the method described in "Nippon Kagaku Kai Shi", No. 1, 1980, pp.74-78).

That is, peak ratio based on methyl group and methylene group in proton nuclear magnetic resonance spectrum is obtained. Separately, the vinyl acetate content is obtained by saponification method and the number average molecular weight is obtained by vapor pressure osmotic pressure method. The degree of branching is calculated from the peak ratio, the vinyl acetate content and the number average molecular weight. It is to be noted that assumption is made that both the ends of the main-chain methylene groups are methyl groups and that all the side chains are ethyl groups, and therefore, 2 terminal methyl groups are deduced upon calculation.

The amount of the cold flowability improver used in this invention is in the range of preferably 30 to 1,500

ppm, more preferably 50 to 1,000 ppm based on the weight of the base fuel oil composed of the middle and/or heavy distillates of petroleum.

When the amount of addition is below 30 ppm, decrease in cold filter plugging point is hardly expectable, while with the amount of addition above 1,500 ppm, economical advantage as compared with the results obtained is poor, which is undesirable.

The fuel oil composition of this invention may contain one or more of rust preventives, antioxidants, antistatics, cetane value improvers and anticorrosives.

5

EXAMPLES

10

Hereinafter, the fuel oil composition of this invention will be explained concretely by way of examples. However, this invention should not be construed as being limited thereto.

Various analyses and measurements of test oils were performed by the following methods. (1) Specific density JIS K2249 (1986)

15

(2) Kinematic viscosity JIS K2283 (1986)

(3) Distillation test JIS K2254 (1986)

(4) Cloud point JIS K2269 (1986)

(5) Pour point JIS K2269 (1986)

20

(6) CFPP (cold filter plugging point):

Measured using an automated cold filter plugging point tester (A4F2 type manufactured by Yoshida Kagaku Kikai Co., Ltd. according to Cold Filter Plugging Point of Distillate Fuels shown in IP-309 (1976, United Kingdom) (7) Amount of wax separated out:

25

In 50 g of a test oil was dissolved 200 ppm of a cold flowability improver (STABINOL FI-18 (registered trademark), commercially available from SUMITOMO CHEMICAL CO., LTD) and the solution was cooled in a 100 ml graduated cylinder from room temperature to -5 °C, -10 °C, or a temperature 10 °C below the cloud point at a rate of 1 °C/hr. Oil component other than wax separated out from the cooled test oil was each removed under vacuum through a filter metal fitting to which 5 µm membrane filter is attached, and 50 ml of cold ethanol/ethyl ether (2/1 by volume) was added to the residual wax component, followed by gentle stirring and then removal of oil component under vacuum.

30 -

Further, 50 ml of cold ethanol was added to the residual wax component and the mixture was all introduced into 11G4 glass filter to remove oily component under vacuum. After the wax component which remained on the glass filter was air-dried for one day and one night, the weight of wax component was measured to obtain the amount of wax separated out. (8) n-Paraffin content:

35

The content of n-paraffin in the test oil was obtained using GAS CHROMATOGRAPH GC-9A type and CHROMATOPACK C-R2AX data processor, manufactured by Shimazu Seisakusho Co., Ltd. n-Triacontane was used as an inner standard substance for quantitative determination. Principal operational conditions are as follows.

40

Column: Made of stainless steel, 3 mm in inner diameter and 4m in length

Column filler:

Silicon GE SE-30 (manufactured by Wako Pure Chemicals Industry, Ltd.), 2%, 60/80 mesh (Uniport HP carrier)

Injection Temperature: 270 °C

Carrier Gas: Helium

45

Detector: Hydrogen flame ionizing detector

Column temperature elevation rate: 5 °C/min. (70 → 270 °C)

46

Example 1

50

To Diesel gas oil samples Nos. 1 to 4 of which characteristics are shown in Tables 1 and 2 were added 500 ppm of a cold flowability improver composed of a 50 wt.% xylene solution of various cold flowability improving substances, and CFPP was measured.

The results of evaluation of the effect by temperature decrease from CFPP of the sample oil itself (Δ CFPP) are shown in Table 3.

55

60

65

Table 1

<u>Sample No.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Specific Density (15/4°C)	0.8290	0.8340	0.8480	0.8521
Kinematic Viscosity (30°C) cSt	4.899	4.556	5.685	5.981
Distillation Test (°C)				
Initial Boiling Point	191	175	244	206
10% Boiling Point	236	229	275	246
90% Boiling Point	346	342.5	327	356.5
Dry Point	368	364	338	382
Cloud Point (CP) °C	0	-3	-6	2
Pour Point °C	-5	-7.5	-10	-10
CFPP °C	-3	-5	-8	-7
Amount of Wax Separated Out (wt%)				
-5°C	0.84	0.62	0.00	1.21
-10°C	1.86	1.75	2.25	2.35
CP-10°C	1.86	2.65	4.63	2.95

Note: CP-10°C is a temperature 10°C below the cloud point

Table 2

<u>Carbon Number of n-Paraffin</u>	<u>n-Paraffin Content (wt. %)</u>			
	<u>No. 1</u>	<u>No. 2</u>	<u>No. 3</u>	<u>No. 4</u>
10	0.04	0.04	0.03	0.00
11	0.63	0.58	0.12	0.00
12	0.68	0.68	0.15	0.10
13	0.88	0.92	0.40	0.34
14	1.51	1.42	0.82	1.59
15	1.94	2.17	1.71	1.20
16	2.30	2.59	3.13	1.73
17	3.40	2.90	4.98	1.56
18	2.42	2.57	3.52	1.55
19	1.54	1.63	2.19	1.46
20	1.23	1.23	1.51	1.30
21	0.81	0.77	0.75	0.84
22	0.61	0.54	0.42	0.73
23	0.41	0.36	0.18	0.46
24	0.27	0.22	0.10	0.38
25	0.16	0.15	0.02	0.27
26	0.10	0.08	0.02	0.16
27	0.05	0.03	0.00	0.11
28	0.02	0.01	0.00	0.06
29	0.00	0.00	0.00	0.02
Total of C25≤	0.33	0.27	0.04	0.62

Note: "Total of C25≤" indicates total of n-paraffin having at least 25 carbon atoms.

Table 3

5

10	Run No.	Cold Flow Improver	$\Delta CFPP$ (°C)			
			No. 1	No. 2	No. 3	No. 4
15	1	EVA Copolymer (VA 34 wt.%, Mn 1630)	12	7	0	0
20	2	EVA Copolymer (VA 28 wt.%, Mn 2050)	10	5	0	0
25	3	EVA Copolymer (VA 29 wt.%, Mn 2100)	8	4	0	0
	4	EVA Copolymer (VA 18 wt.%, Mn 2300)	4	0	0	0

Table 3 (continued)

30	Run No.	M.W. Distribution	Number of Methyl Terminated Side Chain (groups/100 methylene groups)
35	1	2.2	3.6
	2	2.8	7.2
40	3	4.4	3.8
	4	2.4	5.9

45 Notes: "VA" stands for vinyl acetate, and "Mn" indicates number average molecular weight.

50

55

Example 2

60 Diesel gas oil samples Nos. 5 and 9 shown in Tables 4 and 5 were mixed with each other at a mixing ratio of 75/25 (Sample No. 6), 50/50 (Sample No. 7), or 25/75 (Sample No. 8), each by volume. The characteristics of mixed test oils are also shown in Tables 4 and 5.

65 To these sample oils were added 300 ppm or 500 ppm of Additive A composed of a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 36.5 wt.%, a number average molecular

weight of 1,690, and a number of methyl terminated side chains of 3.8 groups/100 methylene groups, and CFPP of each mixture was measure.

The results of evaluation of the effect by temperature decrease from CFPP of the sample oil itself (Δ CFPP) are shown in Table 6 and Fig. 2.

5

Table 4

Sample No.	5	6	7	8	9
Specific Density (15/4°C)	0.8405	0.8405	0.8410	0.8410	0.8410
Kinematic Viscosity (30°C) cSt	4.582	4.542	4.517	4.430	4.387
Distillation Test (°C)					
Initial Boiling Point	201.5	200	207	214	215
10% Boiling Point	238	240	239	240	242
90% Boiling Point	342	341	340.5	335	330
Dry Point	371	368	363	356	351
Cloud Point (CP) °C	1	0	-2	-2	-2
Pour Point °C	-5	-5	-7.5	-7.5	-7.5
CFPP °C	-1	-3	-3	-4	-5
Amount of Wax Separated Out (wt%)					
-5°C	0.90	0.82	0.77	0.61	0.53
-10°C	1.64	1.81	2.05	2.32	2.58
CP-10°C	1.52	1.81	2.54	2.93	3.41

Note: CP-10°C is a temperature 10°C below the cloud point.

50

55

60

65

Table 5

<u>Carbon Number of n-Paraffin</u>	<u>n-Paraffin Content (wt.%)</u>				
	<u>No. 5</u>	<u>No. 6</u>	<u>No. 7</u>	<u>No. 8</u>	<u>No. 9</u>
10	0.30	0.23	0.21	0.20	0.14
11	0.61	0.56	0.53	0.51	0.42
12	0.93	0.90	0.85	0.83	0.81
13	1.78	1.89	1.95	2.10	2.14
14	2.61	2.59	2.59	2.61	2.61
15	2.49	2.58	2.63	2.67	2.72
16	2.29	2.47	2.58	2.64	2.67
17	2.42	2.83	3.06	3.41	3.64
18	2.20	2.44	2.58	2.67	2.81
19	1.45	1.55	1.66	1.78	1.88
20	1.13	1.21	1.32	1.40	1.44
21	0.81	0.85	0.92	0.96	1.01
22	0.69	0.73	0.77	0.80	0.84
23	0.47	0.50	0.50	0.50	0.52
24	0.31	0.31	0.32	0.31	0.30
25	0.28	0.25	0.20	0.14	0.11
26	0.13	0.11	0.10	0.05	0.05
27	0.06	0.05	0.03	0.00	0.00
28	0.01	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00
Total of C25≤	0.48	0.41	0.33	0.19	0.15

Notes: "Total of C25≤" indicates total of n-paraffin having at least 25 carbon atoms.

Gas chromatogram of sample oil No. 5 is shown in Fig. 1.

Table 6

Sample No.	Δ CFPP (°C)					10
	5	6	7	8	9	
<u>Amount of Addition</u>						
300 ppm	2	7	4	1	0	15
500 ppm	3	12	8	2	1	20

Example 3

To sample fuel oils shown in Table 7 was added 500 ppm of Additive A described in Example 2, and CFPP was measured.

The results of evaluation of the effect by temperature decrease from CFPP of the sample fuel oil itself (Δ CFPP) are shown in Table 7 and also in Fig. 2.

Further, for comparison, results obtained using Additive B and Additive C are shown in Table 7 and Figs. 3 and 4.

Additive B is a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 16.5 wt.%, a number average molecular weight of 2,200.

Additive C is a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 44.6 wt.% and a number average molecular weight of 1,820.

30

35

39

40

45

50

55

60

65

Table 7

<u>Sample No.</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>
Specific Density (15/4°C)	0.8510	0.8444	0.8488	0.8467	0.8418
Kinematic Viscosity (30°C) cSt	5.293	4.895	4.379	4.887	4.131
Distillation Test (°C)					
Initial Boiling Point	197	197	168	210	162.5
10% Boiling Point	259.5	249.5	234	259	216
90% Boiling Point	338	338.5	337	332	343
Dry Point	363	364.5	354	351	362
Cloud Point (CP) °C	-1	-3	-6	-5	-5
Pour Point °C	-2.5	-5	-7.5	-7.5	-7.5
CFPP °C	-3	-3	-6	-5	-5
Amount of Wax Separated Out (wt%)					
-5°C	1.22	0.88	0.00	0.00	0.00
-10°C	2.75	2.03	1.96	2.10	1.80
CP-10°C	3.21	2.46	5.13	4.61	3.90
Content of n-Paraffin (°C)					
Total	20.63	21.07	19.68	21.77	19.42
C20≤	4.21	3.85	3.69	3.44	3.81
C25≤	0.21	0.22	0.05	0.04	0.10
Δ CFPP (°C)					
Additive A	2	3	0	0	1
Additive B	0	1	0	0	0
Additive C	0	1	0	0	0

Note: CP-10°C is a temperature 10°C below the cloud point.

Table 7 (Continued)

<u>Sample No.</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>
Specific Density (15/4°C)	0.8463	0.8290	0.8340	0.8450	0.8550
Kinematic Viscosity (30°C) cSt	4.050	2.960	4.556	4.720	4.511
Distillation Test (°C)					
Initial Boiling Point	166	191	175	207	208.5
10% Boiling Point	224	236	229	253.5	250.5
90% Boiling Point	334	346	342.5	325.5	318
Dry Point	353	368	364	342	337
Cloud Point (CP) °C	-5	0	-3	-11	-12
Pour Point °C	-7.5	-5	-7.5	-12.5	-12.5
CFPP °C	-5	-3	-5	-11	-13
Amount of Wax Separated Out (wt%)					
-5°C	0.00	0.84	0.62	0.00	0.00
-10°C	1.65	1.68	1.75	0.00	0.00
CP-10°C	3.55	1.68	2.41	5.23	6.71
Content of n-Paraffin (°C)					
Total	20.18	19.63	19.26	17.69	18.60
C20≤	3.52	3.70	3.37	2.02	1.52
C25≤	0.04	0.36	0.24	0.01	0.00
Δ CFPP (°C)					
Additive A	0	11	8	0	0
Additive B	0	3	3	0	0
Additive C	0	3	3	0	0

Note: CP-10°C is a temperature 10°C below the cloud point.

Table 7 (Continued)

Sample No.	20	21	22	23	24
Specific Density (15/4°C)	0.8485	0.8472	0.8510	0.8630	0.8615
Kinematic Viscosity (30°C) cSt	5.482	5.469	5.349	5.202	5.216
Distillation Test (°C)					
Initial Boiling Point	234	224.5	221	204	207
10% Boiling Point	265	263.5	240	247	245
90% Boiling Point	328	325	345	360.5	362
Dry Point	348	340	367	381	381
Cloud Point (CP) °C	-2	-2	4	7	7
Pour Point °C	-5	-7.5	-2.5	0	1
CFPP °C	-5	-5	-4	0	0
Amount of Wax Separated Out (wt%)					
-5°C	0.26	0.61	1.13	1.70	1.65
-10°C	3.13	3.09	3.78	-	-
CP-10°C	3.62	4.11	0.91	1.21	0.74
Content of n-Paraffin (°C)					
Total	24.46	25.30	21.81	13.98	16.69
C20≤	3.61	3.42	4.50	3.98	4.36
C25≤	0.23	0.11	0.46	0.78	0.67
Δ CFPP (°C)					
Additive A	3	0	8	0	0
Additive B	1	0	2	0	0
Additive C	0	0	2	0	0

Note: CP-10°C is a temperature 10°C below the cloud point.

Table 7 (Continued)

<u>Sample No.</u>	<u>25</u>
Specific Density (15/4°C)	0.8602
Kinematic Viscosity (30°C) cSt	4.613
Distillation Test (°C)	
Initial Boiling Point	190
10% Boiling Point	250
90% Boiling Point	335
Dry Point	359
Cloud Point (CP) °C	0
Pour Point °C	-2
CFPP °C	-2.5
Amount of Wax Separated Out (wt%)	
-5°C	2.06
-10°C	4.32
CP-10°C	4.32
Content of n-Paraffin (°C)	
Total	20.77
C ₂₀ ≤	4.22
C ₂₅ ≤	0.27
Δ CFPP (°C)	
Additive A	0
Additive B	0
Additive C	0

Note: CP-10°C is a temperature 10°C below the cloud point.

EFFECT OF THE INVENTION

5

As evident from the above-described examples, sample oils which contained n-paraffin having at least 25 carbon atoms in an amount of below 0.1 wt.% or not smaller than 0.6 wt.% and wax component which separated out at a temperature 10°C below the cloud point in an amount of not smaller than 4 wt.% did not exhibit effect of decreasing CFPP by the addition of a cold flowability improver. In contrast, those oils which contained n-paraffin in an amount of not smaller than 0.1 wt.% and below 0.6 wt.% and wax component which separated out at a temperature 10°C below the cloud point in an amount of below 4 wt. % showed decrease in CFPP with the cold flowability improver. This effect was much more excellent with sample oils of which the wax content was not smaller than 0.2 wt.% and below 0.5 wt.%.

Further, CFPP of fuel oils decreased widely particularly when an ethylene-vinyl acetate copolymer having an ethylene content of 60 to 80 wt.% and a number average molecular weight of 1,000 to 4,000 was used as a cold flowability improver. Among them, remarkable effect was observed with those copolymers which had a molecular weight distribution of not greater than 4.0 and contained not more than 6 methyl terminated side chains per 100 methylene units.

20

Claims

25

1. A fuel oil composition comprising a base fuel oil composed mainly of middle and/or heavy distillates of crude oil and containing n-paraffin having at least 25 carbon atoms in an amount of not smaller than 0.1 wt.% and smaller than 0.6 wt.% and wax which separates out at a temperature by 10°C lower than the cloud point in an amount of smaller than 4 wt.%, and a cold flow improver composed of a copolymer of ethylene and a vinyl ester of an unsaturated carboxylic acid, the copolymer having an ethylene content of 60 to 80 wt.% and a number average molecular weight of 1,000 to 5,000, in an amount of 30 to 1,500 ppm.

30

2. The fuel oil composition as claimed in Claim 1, wherein said n-paraffin is contained in an amount of not smaller than 0.2 wt.% and smaller than 0.5 wt.%.

35

3. The fuel oil composition as claimed in Claim 1, wherein said vinyl ester of the unsaturated carboxylic acid is vinyl acetate.

40

4. The fuel oil composition as claimed in Claim 3, wherein said copolymer of ethylene and vinyl acetate has an ethylene content of 60 to 75 wt.%, a number average molecular weight of 1,000 to 4,000, and a molecular weight distribution of not greater than 4.0, and contains not more than 6 methyl terminated side chains per 100 main chain methylene units in addition to methyl groups contained in the acetyl groups thereof.

45

50

55

60

65

0301837

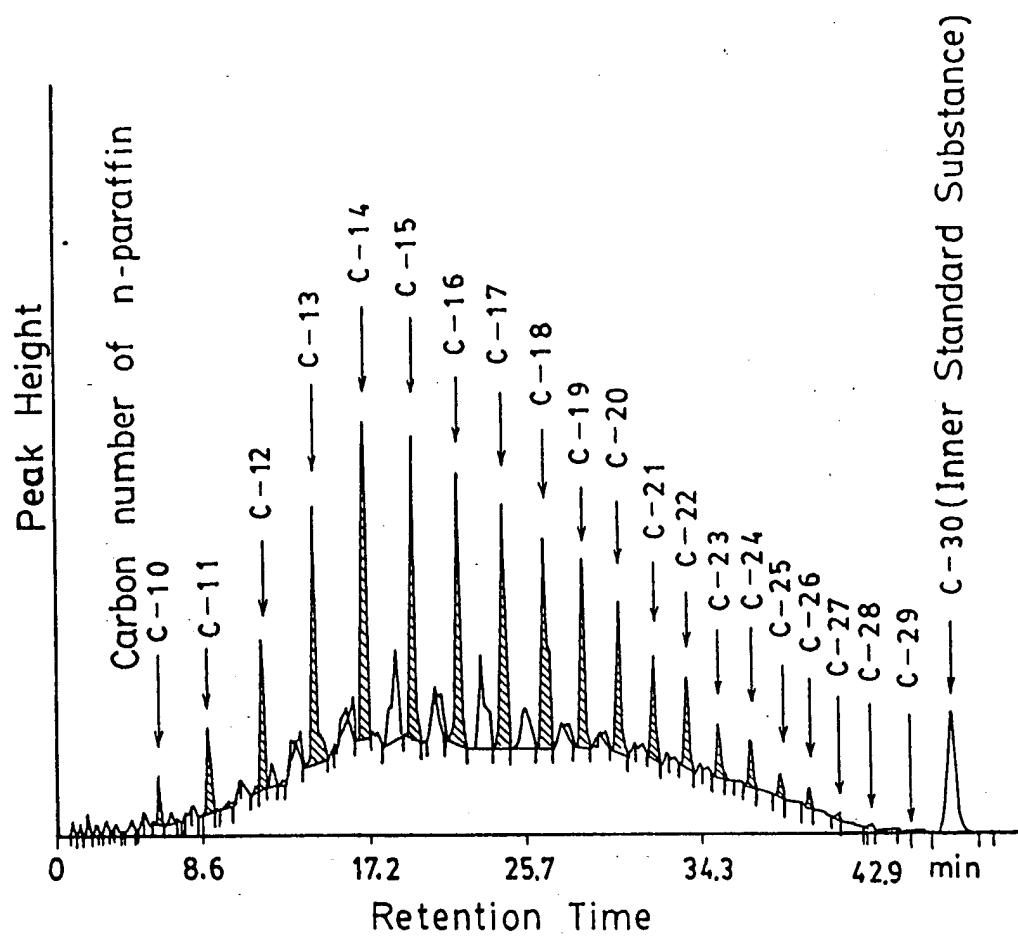


FIG. 1

0301837

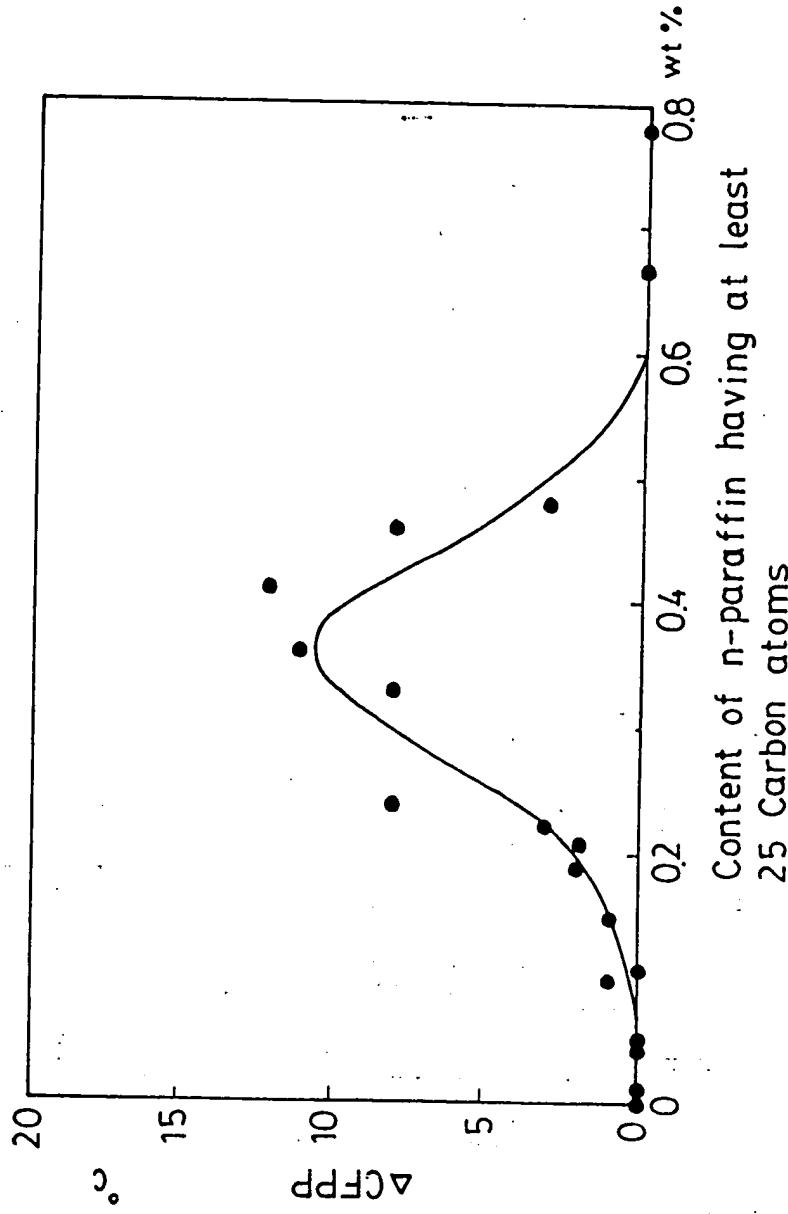


FIG. 2

0301837

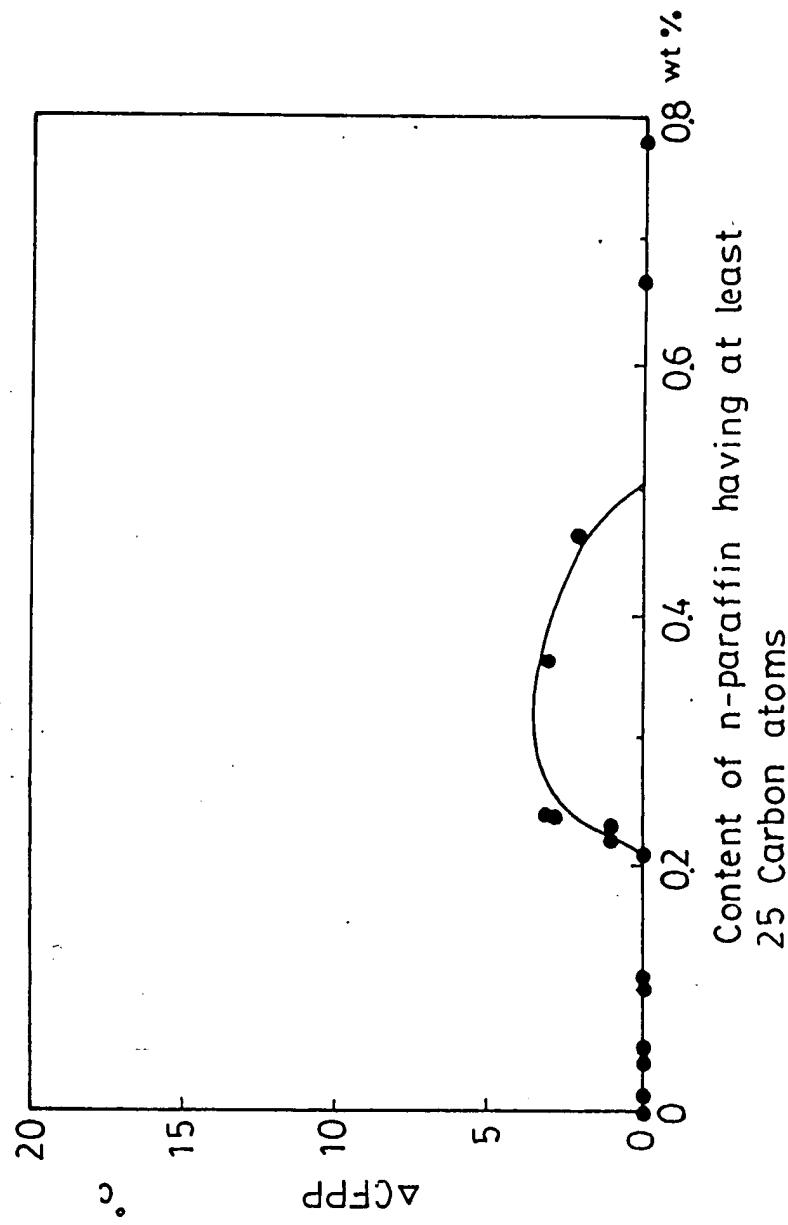


FIG. 3

0301837

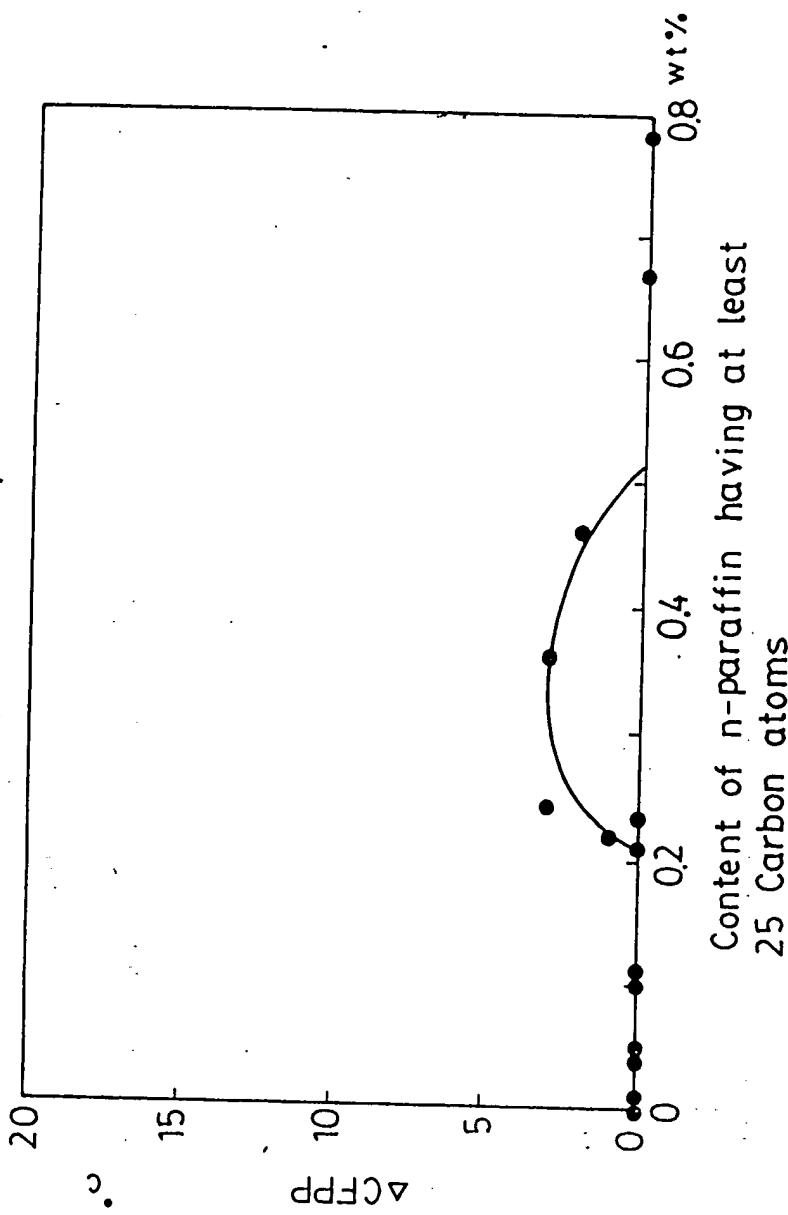


FIG. 4



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 30 6929

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-4 354 011 (ILNYCKYJ) * Whole document * ---	1-4	C 10 L 1/14
X	US-A-4 210 424 (FELDMAN et al.) * Whole document * ---	1-4	
X	GB-A-1 264 684 (ESSO RESEARCH & ENGINEERING CO.) * Whole document * ---	1,3	
A	---	2,4	
X	FR-A-2 307 032 (EXXON RESEARCH & ENGINEERING CO.) * Whole document * ---	1,3	
X	.	2,4	
X	EP-A-0 061 895 (EXXON RESEARCH & ENGINEERING CO.) * Claims; pages 17,20,21 * ---	1,3	
A	---	2,4	
X	GB-A-1 264 638 (ESSO RESEARCH & ENGINEERING CO.) * Whole document * ---	1,3	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	---	2,4	C 10 L
X	EP-A-0 187 488 (EXXON RESEARCH & ENGINEERING CO.) * Whole document * ---	1-4	
X	EP-A-0 184 048 (NAT. DISTILLERS & CHEMICAL CORP.) * Claim * ---	1,3	
		-/-	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	27-09-1988	DE LA MORINERIE B.M.S.B.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date		
A : technological background	D : document cited in the application		
O : non-written disclosure	L : document cited for other reasons		
P : intermediate document	& : member of the same patent family, corresponding document		



European Patent
Office

EUROPEAN SEARCH REPORT

Page 2

Application Number

EP 88 30 6929

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
A	-----	4	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	27-09-1988	DE LA MORINERIE B.M.S.B.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category.	E : earlier patent document, but published on, or after the filing date		
A : technological background	D : document cited in the application		
O : non-written disclosure	L : document cited for other reasons		
P : Intermediate document	& : member of the same patent family, corresponding document		